

Figure 5. (a) INDO spin densities at endo (▲), exo (●), equatorial (Δ), and axial (○) protons as a function of the conformation of the six-membered ring for an axial NO group. (b) Ratio of these spin densities for protons on the same carbon atom.

and sign (Figures 3, 4a, and 5a). s-Orbital spin densities at endo and equatorial protons are highly dependent both in magnitude and sign on the $>N-O$ conformation (Figures 3 and 4a) and these protons are directly involved in the empirical W-plan description.¹⁷ A boat conformation ($\psi = 220^\circ$) for the six-membered ring is consistent with the experimental signs (Figure 3). On the other hand, a chair conformation ($120^\circ < \psi <$

(17) G. A. Russell in "Radical Ions," E. T. Kaiser and L. Kevan, Ed., Interscience, New York, N. Y., 1968.

160°) gives positive spin density at equatorial protons only for positive φ (Figure 4a). The best fit is obtained for $\varphi = 30^\circ$ (Figure 4b) and $\psi = 120^\circ$ (Figure 5b).¹⁸ Moreover, this conformation has the lowest INDO calculated energy, and the observed hfsc's are in agreement with the W rule.

It may tentatively be concluded that these two radicals have a six-membered ring in a chair conformation, as in the tropinone series,¹⁹ and predominantly an axial N-O group.

Acknowledgment. We wish to thank Y. Ellinger, H. Lemaire, and R. Subra for helpful discussions during this work. We are also indebted to Drs. P. J. Krusic and G. R. Underwood for comments on this paper.

(18) If we assume that radical II has the conformation where $\psi = 120^\circ$ and $\varphi = 30^\circ$, we can estimate the ratio, r_M , of the hfsc (a_M) to calculated s-orbital spin density (ρ^s_M) for a given nucleus M: $r_M = a_M/\rho^s_M$. It is found that for γ protons, $1000 < r_{H\gamma} < 1500$, for β protons $r_{H\beta} \sim 3000$, and for nitrogen $r_N \sim 800$. The quantities are much larger than those given by Pople: $r_H = 539.86$ and $r_N = 379.34$. It is seen that INDO calculations underestimate s-orbital spin densities at γ protons. In our opinion, too much spin density is kept at the two heteroatoms of the "radical center," and this may deserve a new analysis of the N and O INDO parameters for the nitroxide group.

(19) P. Scheiber, G. Kraiss, and K. Nador, *J. Chem. Soc. B*, 1366 (1970), and references cited therein.

Molecular Structure of Bicyclo[2.1.1]hexane

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Abstract: The molecular structure of bicyclo[2.1.1]hexane has been determined by gas-phase electron diffraction. The geometry of this bicyclic compound was determined by resolution of the refined radial distribution curve, followed by a least-squares fitting of the calculated intensity curve to that observed. The structural parameters thus determined are as follows: $C_1-C_3 = 1.544 \pm 0.015$, $C_1-C_2 = 1.565 \pm 0.024$, $C_2-C_3 = 1.513 \pm 0.015$, and $C-H = 1.112 \pm 0.003$ Å and the dihedral angle of the four-membered ring is $125.0 \pm 2.0^\circ$. A comparison of this structure with tricyclo[3.3.0.0^{2,6}]octane has been made in order to check the constancy of some C-C bond lengths.

Several strained polycyclic hydrocarbons have been subjected to structural studies owing to their rigidity and their importance for the discussions of nonbonded interactions, chemical reactivity, and strain energy calculations.¹ Bicyclo[2.1.1]hexane is one of the strained compounds in the series under investigation by the author at this laboratory. It is chosen for this study in order to make a valid, meaningful comparison with the previous determined structure of tricyclo[3.3.0.0^{2,6}]octane,^{1b} and to investigate the constancy of the C-C bond length and the puckering in cyclobutane ring. It is also the purpose of this study to report a concise, true structure of this molecule, since an earlier electron diffraction study² is not conclusive owing to false assumption in the analysis.

(1) (a) J. F. Chiang, C. F. Wilcox, Jr., and S. H. Bauer, *J. Amer. Chem. Soc.*, **90**, 3149 (1968); (b) J. F. Chiang and S. H. Bauer, *Trans. Faraday Soc.*, **64**, 2247 (1968).

(2) G. Dallinga and L. H. Toneman, *Recl. Trav. Chim. Pays-Bas*, **86**, 171 (1967).

Experimental Section

The sample of bicyclo[2.1.1]hexane was furnished by Dr. F. Uno and Professor J. Meinwald of Cornell University. Sector electron diffraction photographs were taken with the apparatus at Professor Bauer's laboratory at Cornell University; it has been described elsewhere.³ Two sets of data were obtained for this compound under the following conditions: 65 kV at a 251.2-mm sample-to-plate distance covered the angular range from $q = 10$ to 38 \AA^{-1} , and 65 kV, 124.1 mm, covered the range $q = 26$ to 128 \AA^{-1} ($q = (40/\lambda) \sin \theta/2$). MgO diffraction patterns were concurrently recorded for scale factors. The scattering patterns were microphotometered with a double-beam Jarrell-Ash microdensitometer interfaced with a digital recorder. The procedure for data reduction and structure analysis has been described in several previous publications.⁴ The elastic and inelastic form factors of

(3) S. H. Bauer and K. Kimura, *J. Phys. Soc. Jap.*, **17**, 300 (1962); S. H. Bauer, Electron Diffraction Studies at High Temperatures, Report No. Nonr-401(41), Project No. NR092-504, ARPA Order No. 23-53.

(4) J. L. Hencher and S. H. Bauer, *J. Amer. Chem. Soc.*, **89**, 5527 (1967); W. Harshbarger, G. Lee, R. F. Porter, and S. H. Bauer, *Inorg. Chem.*, **8**, 1683 (1969).

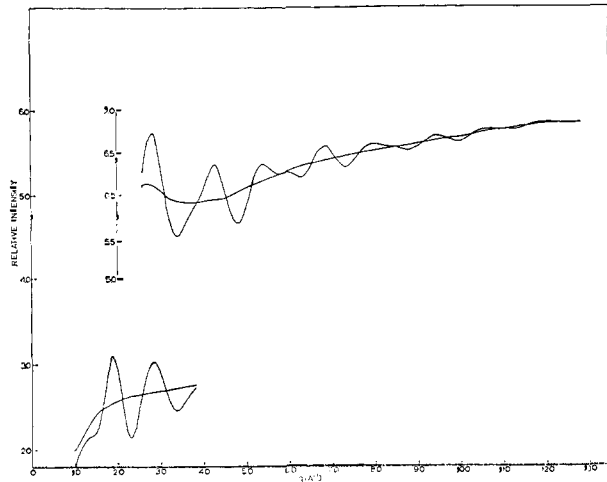


Figure 1. Relative intensities as a function of diffraction angle [$q = (40/\lambda) \sin \theta/2$] for long and short sample-plate distances.

Tavard, *et al.*,⁵ were used in conjunction with the Ibers and Hoerni⁶ phase-shift approximation in the intensity calculations.

Analysis and Results

The experimental intensity and background curves are shown in Figure 1. The theoretical and reduced experimental molecular intensity curves are plotted in Figure 2, along with the difference between them. Figure 3 shows the final experimental radial distribution curve, where the lower oscillating curve is the difference between the experimental function and the theoretical radial distribution function calculated from the final best model.

In Figure 3, the radial distribution curve, the first peak is due to all bonded C-H distances, while the second peak is a superposition of the following bonded carbon-carbon distances: C₂-C₃ = 1.513, C₁-C₅ = 1.544, and C₁-C₂ = 1.565 Å. The third peak centered at $r = 2.37$ Å is contributed by all carbon-carbon nonbonded distances, C₅---C₆ = 1.946, C₁---C₄ = 2.172, C₂---C₅ = 2.381, and C₁---C₃ = 2.395 Å and some nonbonded C-H and H-H distances. The last peak at $r = 3.34$ Å is due to some further separated nonbonded C---H and H---H distances.

Table I. Coordinates of Bicyclo[2.1.1]hexane

	X	Y	Z
C ₁	1.0860	0.0	1.5299
C ₂	0.7565	0.0	0.0
C ₃	-0.7565	0.0	0.0
C ₄	-1.0860	0.0	1.5299
C ₅	0.0	-0.9731	2.0369
C ₆	0.0	0.9731	2.0369
H ₇	2.1937	0.0	1.6327
H ₈	1.1103	0.9594	-0.4381
H ₉	1.1103	-0.9594	-0.4381
H ₁₀	-1.1103	0.9594	-0.4381
H ₁₁	-1.1103	-0.9594	-0.4381
H ₁₂	-2.1937	0.0	1.6327
H ₁₃	0.0	-1.6582	2.9134
H ₁₄	0.0	1.7063	1.2002
H ₁₅	0.0	1.6582	2.9134
H ₁₆	0.0	1.7063	1.2002

(5) C. Tavard, D. Nicholas, and M. Rouault, *J. Chim. Phys. Physicochim. Biol.*, **64**, 540 (1967).

(6) J. A. Ibers and J. A. Hoerni, *Acta Crystallogr.*, **7**, 405 (1954).

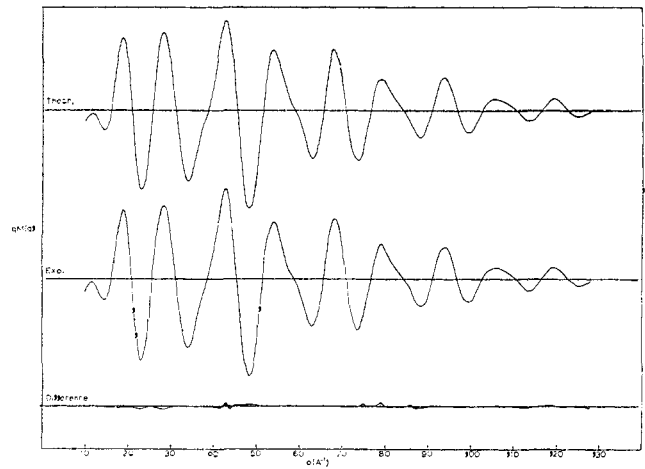


Figure 2. The experimental and theoretical $qM(q)$ curves; the lower oscillating curve is the difference between the theoretical and experimental curves.

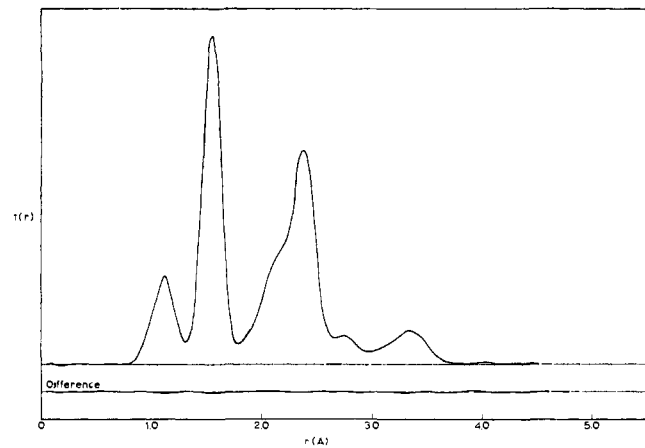


Figure 3. Experimental radial distribution curve and the difference between the experimental and theoretical curves for the best model.

The structure of bicyclo[2.1.1]hexane is shown in Figure 4. Coordinates of the molecule are shown in Table I. C_{2v} symmetry was assumed for calculating the geometry of the molecule. The following geometrical parameters were used for calculations: C₁-C₂, C₂-C₃, C₁-C₅, C-H, C₁---C₄, C₅---C₆, $\angle H_8C_2H_9$, θ (the angle between C₁-C₄ and C₁-H₇), α (the angle between C₅-H₁₃ and the y axis), and β (the angle between C₅-H₁₄ and the y axis). Models of C_{2v} symmetry with various combinations of geometrical parameters were tested before the execution of the least-squares program. The final values of these parameters and some mean amplitudes

Table II. The Geometrical Parameters for Bicyclo[2.1.1]hexane

C ₁ -C ₂ , Å	1.565 ± 0.024	0.0607 ± 0.0021
C ₁ -C ₅ , Å	1.544 ± 0.015	0.0607 ± 0.0021
C ₂ -C ₃ , Å	1.513 ± 0.015	0.0607 ± 0.0021
$\langle C-H \rangle_{av}$, Å	1.112 ± 0.005	0.095 ^a
C ₁ ---C ₄ , Å	2.172 ± 0.016	0.090 ^a
C ₅ ---C ₆ , Å	1.946 ± 0.011	0.129 ± 0.010
$\angle H_8C_2H_9$, deg	109.2 ± 4.0	
θ , deg	5.3 ± 4.2	
α , deg	52.0 ± 3.0	
β , deg	48.8 ± 2.0	

^a Assumed values.

Table III. Error Matrix

	C ₂ -C ₃	C ₁ -C ₂	C ₁ -C ₃	C-H	∠H ₈ C ₂ H ₉	C ₁ ---C ₄	θ	α	β	C ₅ ---C ₆	IC-C	IC ₂ -C ₅	IC ₃ -C ₆
C ₂ -C ₃	0.0046												
C ₁ -C ₂	0.0053	0.0088											
C ₁ -C ₃	-0.0040	-0.0064	0.0047										
C-H	0.0010	0.0014	-0.0010	0.0007									
∠H ₈ C ₂ H ₉	0.0290	0.0451	-0.0326	0.0083	0.3467								
C ₁ ---C ₄	-0.0044	-0.0067	0.0049	-0.0012	-0.0314	0.0055							
θ	0.0624	0.0939	-0.0662	0.0190	0.5747	-0.0738	1.3770						
α	-0.0416	-0.0680	0.0494	-0.0096	-0.4307	-0.0452	-0.8726	0.9959					
β	0.0467	0.0699	-0.0505	0.0145	0.3385	-0.0554	+0.8907	-0.6107	0.6882				
C ₅ ---C ₆	0.0032	0.0042	-0.0030	0.0009	0.0137	-0.0040	0.0504	-0.0105	0.0384	0.0037			
IC-C	-0.0012	-0.0025	0.0018	-0.0004	-0.0124	0.0018	-0.0254	0.0191	-0.0190	-0.0010	0.0007		
IC ₂ -C ₅	-0.0007	-0.0009	0.0007	-0.0002	-0.0052	0.0005	-0.0092	0.0108	-0.0088	0.0001	0.0002	0.0004	
IC ₃ -C ₆	0.0030	0.0055	-0.0039	0.0010	0.0308	-0.0040	0.0702	-0.0533	0.0541	0.0021	-0.0016	-0.0008	0.0058

of vibrations were refined by applying a least-squares program on the reduced molecular intensity. A starting set of parameters based on the structure of Dallinga, *et al.*,² was also tested with the least-squares refinement

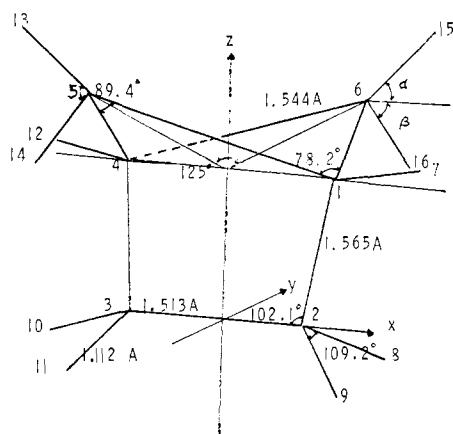


Figure 4. The structure of bicyclo[2.1.1]hexane.

program. Without imposing any constraint on the geometrical parameters, the set converged after 15 cycles to the same structure as we obtained previously. The final values of the geometrical parameters from the least-squares analysis are listed in Table II. The error matrix is shown in Table III. The assigned uncertainties in Table II are three times the calculated standard deviations which are the diagonal elements of the error matrix.

Discussion

The structure of bicyclo[2.1.1]hexane derived from this study shows several interesting features as compared with a similar but more rigid molecule, tricyclo[3.3.0.0^{2,6}]octane.^{1b} A comparison of bicyclo[2.1.1]hexane, bicyclo[2.1.1]-2-hexene,⁷ and tricyclo[3.3.0.0^{2,6}]octane is shown in Table IV. As seen in Table IV, all C-C bond lengths in bicyclo[2.1.1]hexane have the same magnitudes as the corresponding C-C bond lengths in the tricyclic compound. One may view this as follows: the attachment of an ethylenic group (-CH₂-CH₂) to C₅, C₆ of bicyclo[2.1.1]hexane gives the tricyclic compound with unchanged C-C bond lengths. The dihedral angles of all these three substituted puckered

(7) J. F. Chiang and S. H. Bauer, manuscript in preparation; Abstracts, 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1970, No. PHYS 106.

Table IV. Comparison of the Structures of Bicyclo[2.1.1]hexane, Bicyclo[2.1.1]-2-hexene, and Tricyclo[3.3.0.0^{2,6}]octane

	Bicyclo-[2.1.1]-hexane	Bicyclo[2.1.1]-2-hexene	Tricyclo-[3.3.0.0 ^{2,6}]-octane
C ₁ -C ₂ , Å	1.565	1.537	1.569
C ₂ -C ₃ , Å	1.513	1.332 (C=C)	1.516
C ₁ -C ₃ , Å	1.544	1.549	1.558
∠C ₁ C ₂ C ₃ , deg	102.1	108.4	100.2
α, α deg	125.0	123.5	126.7

^a α is the dihedral angle of the four-membered ring.

four-membered rings are very close to each other, 125.0° for bicyclohexane, 123.5° for bicyclohexene, and 126.7° for tricyclooctane. The C-C bond length (1.544 Å) in the cyclobutane ring of bicyclohexane is identical with that in bicyclo[1.1.1]pentane (1.545 Å).⁸ The dihedral angle of the former (125.0°) is not far from that of the latter (120°). The C-C distance in the four-membered ring of bicyclohexane also agrees with that in the unsubstituted cyclobutane.⁹

Another comparison is made for the five-membered ring in bicyclohexane and the unsubstituted cyclopentane. The average C-C bond length of the former (1.546 Å) is in complete agreement with that of the latter (1.546 Å).¹⁰ This value is longer than a normal C-C bond in ethane¹¹ and *n*-alkanes¹² by 0.012 Å.

The structure of bicyclo[2.1.1]hexane reported by Dallinga, *et al.*,² is of questionable value owing to the false assumption made in the structural analysis. In the analysis, the authors assumed that "the difference of 0.01 Å in C-C bond length between cyclobutane and cyclopentane seems to be a well-established experimental fact." This is obviously not the case. The reported C-C distances in cyclobutane⁹ and cyclopentane¹⁰ are 1.548 and 1.546 Å, respectively. This assumption reduced the independent parameters for determining the carbon skeleton of bicyclo[2.1.1]hexane to one bond length and two bond angles. It is usually possible to obtain a fast convergence in a least-squares program with fewer variables, but the parameters thus

(8) J. F. Chiang and S. H. Bauer, *J. Amer. Chem. Soc.*, **92**, 1514 (1970).

(9) A. Almennigen and O. Bastiansen, *Acta Chem. Scand.*, **15**, 711 (1961).

(10) W. J. Adams, H. J. Geise, and L. S. Bartell, *J. Amer. Chem. Soc.*, **92**, 5013 (1970).

(11) L. S. Bartell and H. W. Higginbotham, *J. Chem. Phys.*, **42**, 851 (1965).

(12) R. A. Bonham, L. S. Bartell, and D. A. Kohl, *J. Amer. Chem. Soc.*, **81**, 4765 (1959).

Table V. The Constancy of the C-C Bond Length in Cyclobutane Rings

Compound	C-C (Å)	Reference
Bicyclo[2.1.1]hexane	1.544	This study, electron diffraction
Bicyclo[2.1.1]-2-hexene	1.549	Electron diffraction ^a
Cyclobutane	1.548	Electron diffraction ^b
Tricyclo[3.3.0.0 ^{2,6}]octane	1.558	Electron diffraction ^c
Bicyclo[3.1.1]heptane	1.553	Electron diffraction ^d
Biscyclobutyl	1.548	Electron diffraction ^e
Bicyclo[1.1.1]pentane	1.545	Electron diffraction ^f

^a See ref 7. ^b See ref 9. ^c See ref 1b. ^d G. Dallinga and L. H. Toneman, *Recl. Trav. Chim. Pays-Bas*, **88**, 185 (1969). ^e A. De-Meijere, *Acta Chem. Scand.*, **20**, 1093 (1965). ^f See ref 8.

obtained might not be the true ones. Owing to the above-mentioned reason, a comparison between the two structure determinations seems to be of little significance.

One may conclude that the C-C bond length (1.545 Å) in an unsubstituted cyclobutane ring and any substituted cyclobutane ring was constant, except for those rings with high electronegative substituents. Further support for this conclusion is shown in Table V. A surprisingly small \angle HCH (100.8°) at C₅, C₆ has been found for this molecule and some other strained hydrocarbons.^{7,8}

Acknowledgment. A summer faculty fellowship awarded to the author by the Research Foundation of the State University of New York for part of this study is acknowledged. The author wishes to thank Professor S. H. Bauer for the use of the electron diffraction equipment, Professor J. Meinwald and Dr. Uno for furnishing the sample, and Dr. A. Andreassen for help in the experimental part of this study. Support from Public Health Service Grant No. 1-R01-CA11537-01A1 is also appreciated.

Molecular Complexes of Iodine with Alkyl- and Chloro-Substituted Phosphine Sulfides

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Abstract: Absorption spectrophotometric studies have been made in the near-ultraviolet and visible spectral regions on the iodine complexes of trioctylphosphine sulfide, diethylchlorophosphine sulfide, and trichlorophosphine sulfide, with *n*-heptane as solvent. For the iodine complexes with trioctylphosphine sulfide and diethylchlorophosphine sulfide the charge-transfer band was located in the near-ultraviolet and employed in the evaluation of the thermodynamic parameters for 1:1 complex formation. The spectral characteristics for both of these charge-transfer bands were determined. The charge-transfer band for the trichlorophosphine sulfide-iodine complex could not be located. For all three complexes a "blue shift" of the visible iodine band was observed and isosbestic points were obtained. Thermodynamic parameters were evaluated from the shifted visible iodine band data and the spectral characteristics for this band were determined.

During the past two decades, since Benesi and Hildebrand first determined an equilibrium constant for the benzene-iodine complex,¹ quantitative thermodynamic and electronic spectral data have been obtained for a great many iodine complexes involving a rather large variety of both n and π electron donors.² The strength of these iodine complexes, based on their standard enthalpies of formation, varies from about -1 kcal/mol³ to -12 kcal/mol.⁴ Attempts have been made to correlate the electronic spectral properties with complex stability, for both the charge-transfer (CT) band and the "blue-shifted" visible iodine band.⁵

In order to establish trends and to obtain a meaningful correlation between theory and the thermodynamic

and electronic spectral properties of molecular complexes, it would be most useful to have experimental data involving the greatest range of complex stability for a series of structurally similar molecular complexes. One method of obtaining such data would be to investigate a series of complexes involving a common electron acceptor interacting with several different electron donors each containing the same electron donor site. This has been done, for example, with the iodine complexes of a series of aliphatic amines.⁴ However, the donor strength range of this series varied only from the strongest of known iodine complexes to those of intermediate strength and, consequently, did not include the relatively weak iodine complexes, with $K_c < 1.0$. To cover a more complete range of iodine-complex stability, three phosphine sulfides containing alkyl and chloro substituents were selected: trioctylphosphine sulfide, diethylchlorophosphine sulfide, and trichlorophosphine sulfide.

Another reason for the present study was to clarify some ambiguity with regard to the strength of trialkylphosphine sulfide-iodine complexes. For example, a

(1) H. A. Benesi and J. H. Hildebrand, *J. Amer. Chem. Soc.*, **71**, 2703 (1949).

(2) R. Foster, "Organic Charge-Transfer Complexes," Academic Press, New York, N. Y., 1969, pp 396-404.

(3) (a) T. M. Cromwell and R. L. Scott, *J. Amer. Chem. Soc.*, **72**, 3825 (1950); (b) R. M. Keefer and L. J. Andrews, *ibid.*, **77**, 2164 (1955).

(4) H. Yada, J. Tanaka, and S. Nagakura, *Bull. Chem. Soc. Jap.*, **33**, 1660 (1960).

(5) H. Tsubomura and R. P. Lang, *J. Amer. Chem. Soc.*, **83**, 2085 (1961).